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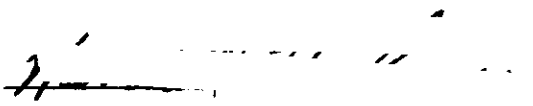

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COMPLEXES OF COBALT(III) WITH TRANS-1,2-CYCLOPENTANEDIAMINE

A THESIS

Presented to

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by

Wendall Hugh Cross

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COMPLEXES OF COBALT(III) WITH

TRANS-1,2-CYCLOPENTANEDIAMINE

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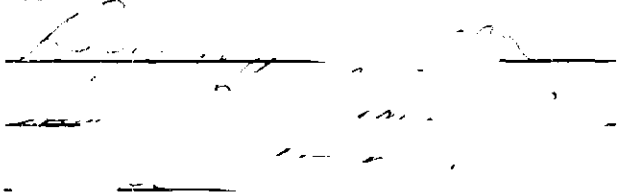

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SUMMARY

The subject of this investigation is the stereochemistry of the cobalt(III) complexes of cis- and trans-cyclopentanediamine. Jaeger and Blumendal made one of the most significant investigations of the stereochemical behavior of complex ions containing asymmetric ligands when they studied the cobalt(III) and rhodium(III) complexes of trans-1,2-cyclopentanediamine (cptdin). The cptdin molecule, having no plane of symmetry, is capable of being resolved into enantiomorphs. Jaeger assumed that cptdin functions as a bidentate ligand and should form eight isomers of the formula $Co(cptdin)_3^{+3}$. However, he was able to isolate only two of the eight isomers, viz., D-$Co(\underline{l}\text{-cptdin})_3^{+3}$ and L-$Co(\underline{d}\text{-cptdin})_3^{+3}$ and in no case could he isolate any mixed complexes of the type $Co(\underline{l}\text{-cptdin})(\underline{d}\text{-cptdin})_3^{+3}$.

In a reinvestigation of this work Royer and Phillips were able to show that cptdin does not function as a bidentate ligand, due to the relatively rigid five-membered carbon ring which prevents formation of an unstrained chelate ring. The complexes which are formed between cobalt(III) and excess cptdin have the formula $Co_2(cptdin)_7(H_2O)_2^{+6}$. In this complex three of the amine molecule function as bidentate ligands by forming bridges between the two cobalt atoms. The remaining four amines are only singly coordinated, two on each cobalt atom. The remaining coordination position on each cobalt atom is occupied by a coordinated water molecule. Royer and Phillips were able to isolate three isomers of this complex which differ only in the relationship of the

coordinated water molecules with respect to each other. They found that the coordinated amine molecules in each complex were of the same optical configuration.

In an extension of the investigation of complexes of cobalt(III) with cptdin two more complex ions have been isolated. The compounds were separated from reaction by-products and other complex ions formed by countercurrent distribution, using water as the stationary phase and n-butanol as the mobile phase. The resulting material from this treatment was then further separated and resolved by fractional crystallization of the d-tartrate salts.

In the complexes which were isolated it was found that the amine to cobalt ratio was always three to one. The first compound on analysis had an approximate overall formula of $\cdot Co(cptdin)_3(CO_3)Cl$. Molecular weight data indicated the compound to be dimeric and the correct formula to be $[Co_2(cptdin)_6(CO_3)]Cl_2$. Investigation of the infrared spectrum shows absorption peaks which can be attributed to bidentate carbonate and the absence of both monodentate carbonate and coordinated water molecules. The visible spectrum shows two maxima, one at 530 millimicrons and the second at 370 millimicrons. The optical rotatory dispersion spectrum of the compound shows a large Cotton effect associated with the 530 millimicron absorption maximum. Although there was insufficient material to allow isolation and characterization of the coordinated amines it is thought that they are all of the same optical configuration due to the large Cotton effect and the high specific rotation of +2400 degrees at 540 millimicrons. A proposed structure for the compound, which would be consistent with the observed data would be one in which there are two

amine molecules bridging the two cobalt atoms and the remaining four amine molecules would be singly coordinated, two on each cobalt atom. The remaining two coordination positions on each cobalt atom would be occupied by the bidentate carbonate groups.

The second compound on analysis had an overall formula of [Co $(cptdin)_3(CO_3)(H_2O)]Cl$. Molecular weight data indicate that this compound is monomeric. Investigation of the infrared spectrum shows the presence of absorption peaks which can be attributed to a bidentate coordinated carbonate and to a coordinated water molecule. The visible spectrum shows two absorption maxima, one at 530 millimicrons and the second at 370 millimicrons. There are several possible structures which can be drawn for this compound. However, the visible spectrum is in good agreement with The β and β' isomers of the tris-aminoacid complexes of cobalt(III) which have all the coordinated oxygens cis to one another. Recovery of the coordinated amine shows that all the amines in a single complex have the same optical configuration. The optical rotatory dispersion spectrum of the complex shows only a plain curve with a low specific rotation of 31 degrees at 540 millimicrons. The entire optical rotation can be attributed to the asymmetric ligand. This is in agreement with the optical activity of the other monodentate optically active ligands whose complexes do not exhibit a Cotton effect in the visible region of the spectra.

Attempts were also made to stereospecifically prepare the cis-1,2-cyclopentanediamine. These were unsuccessful. An attempt was also made to separate the geometrical isomers of the amine by a ligand exchange method employing an ion-exchange column saturated with a nickel ammonia complex. This was also unsuccessful.

CHAPTER I

INTRODUCTION

It is a well established fact that octahedrally coordinated transition metal complexes can exist in optically active forms. It is not necessary for the coordinating ligand itself to be optically active for the complex as a whole to show a high degree of optical activity. Indeed, it was necessary for Werner (1) to synthesize and resolve a complex consisting wholly of elements other than carbon to prove that transition metal complexes could show optical rotations independent of the optical activity of the coordinating ligands.

The stereospecificity, conformation, and stability of the complexes formed from transition metals and various coordinating ligands have been the subject of a great deal of investigation. Werner (2) was able to isolate and characterize all ten isomers of the complex $[Co(en)(pn)(NO_2)_2^+]$ (where en is ethylenediamine and pn is 1,2-propylenediamine). However, most early investigations of coordination compounds which contained optically active ligands led to the isolation of only a very few of the possible isomers. Tschugaef and Sokoloff (3), using optically active 1,2-propylenediamine were able to isolate only two tris-propylenediamine-cobalt (III) salts. The D-$[Co(\underline{d}\text{-pn})_3]Br_3 \cdot 2H_2O$ was obtained from the d-amine while the l-amine yielded only the corresponding L-salt.

Smirnoff (4) confirmed the findings of Tschugaef and Sokoloff in being able to isolate only two salts from the reaction of propylenediamine with cobalt (III). He also observed that reacting $H_2(PtCl_6)$ with

racemic base followed by resolution of the complex formed, yielded only two salts: D-[Pt(l-pn)$_3$]Cl$_4$ and L-[(d-pn)$_3$]Cl$_4$. Reacting $H_2(PtCl_6)$ with l-amine or with d-amine yielded in each case only a single salt.

Jaeger and Blumendal (5) in one of the most important and far reaching investigations of the stereospecificity of optically active ligands used trans-1,2-cyclopentanediamine to form complexes of cobalt (III) and rhodium(III). They reported in each case the formation and resolution of only a single pair of optical isomers, the L-[M(d-cptdin)$_3$] $Cl_3 \cdot 4H_2O$ and D-[M(l-cptdin)$_3$]$Cl_3 \cdot 4H_2O$ (where cptdin is trans-1,2-cyclopentanediamine). In no case did they report the isolation of a salt containing both the dextrorotatory and levorotatory forms of the amine.

Based on his findings and the previous findings concerning propylenediamine and cobalt(III) and platinum(IV), Jaeger attributed the drastic reduction in the number of isolated complexes to a preferred dissymmetrical configuration. That is, the complexes tend to generate the most symmetrical diastereoisomer.

One exception to this stereospecificity is noted. Lifschitz (6) was able to isolate three of the possible four tris-d-alaninecobalt(III) complexes by reacting d-alanine with cobalt(III) hydroxide. He called these α, α', and β and showed that the rotatory dispersion curves of these complexes were quite different.

Jaeger attributed the isolation of the three d-alanine complexes to a greater strength in the alanine chelate ring.

More recently, Douglas and Yamada (7) have been able to prepare the fourth isomer, β', and assign the configuration of each. Denning and Piper (8) have also prepared eleven of the twelve possible isomers

of cobalt (III) with l-alanine, l-leucine, and l-proline. They predict the absence of one isomer of l-proline on steric grounds.

In a series of papers Dwyer and coworkers (9, 10, 11, 12, 13) question the findings of Tschugaef (3) and Smirnoff (4). In addition to describing the preparation of optically pure d- and l-propylenediamine, Dwyer isolated two salts formulated as D-$[Co(d\text{-}pn)_3]I_3 \cdot H_2O$ and L-$[Co(d\text{-}pn)_3]I_3 \cdot H_2O$ having respectively $[\alpha]_D$ + 24 and -214 degrees. He was also able to isolate an isomer believed to be of the type L-Co(lld).

Using Smirnoff's method of preparation, Dwyer isolated two optical isomers of tris-d-propylenediamineplatinum (IV) chloride and a significant amount of bis-d-propylenediamineplatinum(II)chloride. Repeated recrystallizations of the chloride salt yielded L-$[Pt(d\text{-}pn)_3]Cl_4$. He also isolated another isomer D-$[Pt(d\text{-}pn)_3]Cl_4$. In another paper (12) Dwyer and coworkers describe the preparation of the salts L-$[Pt(d\text{-}pn)(d\text{-}pn)_2]Cl_4$ and D-$[Pt(l\text{-}pn)(d\text{-}pn)_2]Cl_4$ by reaction of l-propylenediamine tetrachloroplatinum(IV) with d-propylenediamine followed by resolution of the tartrate salt and regeneration of the chloride salt.

Thus Dwyer has conclusively shown that many of the results derived from previous investigations of propylenediamine coordination compounds are in error. While there may be stereospecific interactions of one propylenediamine with another in a coordination complex, it is not nearly so pronounced as was previously thought.

Corey and Bailar (14) have shown that an isolated nonrigid five-membered chelate ring may adopt one of two conformations, designated k and k' which are enantiomers but energetically equivalent. In the case of tris-ethylenediamine complexes four conformations are possible, vis.,

kkk, kkk', kk'k', k'k'k'. Evaluation of hydrogen-hydrogen interactions leads to a free energy difference of 1.8 Kcal/mole between the most extreme forms. The carbon-carbon bonds in the more stable conformer, designated as kkk, are approximately parallel to the short trigonal axis of the complex, while the carbon-carbon bonds are oblique to the short trigonal axis in the less stable k'k'k' conformer. Thus the kkk conformer is known as the "lel" form while the k'k'k' is known as the "ob' form.

The interpretation of Dwyer's findings are relatively straightforward. The most stable cobalt(III) complexes of propylenediamine are D-$[Co(\underline{d}\text{-pn})_3]^{+3}$ and L-$[Co(\underline{l}\text{-pn})_3]^{+3}$. Propylenediamine may, in principle, form both k and k' chelate rings. The methyl groups must be axial in one ring and equatorial in the other. The energy difference in the two rings, due primarily to steric repulsions of the axial methyl groups, is sufficient to insure the formation of only one type of ring in the complex: k (say) for the dextro propylenediamine and k' for the levo-propylenediamine. As the most stable conformation of octahedral complexes is the lel form, all the propylenediamine molecules will be levo in one configuration and dextro in the other. Because the formation of complexes of the type $[Co(\underline{d}\text{-pn})_2(\underline{l}\text{-pn})]^{+3}$ necessitates that one methyl group be axial and the remaining two equatorial, an equilibrium mixture of cobalt(III) and racemic propylenediamine can be expected to contain relatively minor amounts of such "mixed" complexes.

Royer and Phillips (15) reinvestigated Jaeger's work on the complexes of cobalt(III) with <u>trans</u>-1,2-cyclopentanediamine and were unable to prepare and isolate the previously reported salts. They were able to prepare, isolate and resolve a series of salts which had the same physical

and optical properties as those reported by Jaeger but which had somewhat unusual structures. The overall formulas for the salts were $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$.

In these salts two different types of coordinated amines are present. The structure consists of two cobalt nuclei bridged by three amine molecules and then the remaining amine molecules are singly coordinated; two to each of the cobalts. This structure arises from the fact that the cyclopentane ring forms a rigid base for the two trans-amine groups and it would require a large amount of strain in the cyclopentane ring for normal chelation to occur.

The stereospecificity of the trans-1,2-cyclopentanediamine in the complexes was found to be the same as that reported by Jaeger, that is, all the amines in a single isomer had the same configuration. This can be explained on the basis of steric repulsion which would be encountered if both optical isomers of either the bridging or the singly coordinated amines were present in a single complex ion.

However, if only two bridging amines were present or if all the terminal monodentate amine molecules were of the same configuration and opposite in configuration to the bridging amines it should be possible to form complexes which are stable and contain both the dextro and levo forms of the amine.

In the case of the other geometrical isomer, the cis-1,2-cyclopentanediamine, chelation should occur. However, the chelate ring formed should be a five-membered ring of the envelope conformation with the cobalt atom being the out of plane atom. Hence, a reduction in stability with respect to (say) the ethylenediamine complexes should be observed

due to the greater interactions between the eclipsed hydrogen atoms on the ligand.

It was therefore decided to investigate further the complexes formed when trans-1,2-cyclopentanediamine is reacted with cobalt(III) in hopes of obtaining further information on the stereospecificity of the amine in the complexes formed. It was also hoped that the tris-cis-1,2-cyclopentanediaminecobalt(III) complex could be prepared in order to determine what effect the formation of an almost planar chelate ring has on the stability and properties of the complex ion formed.

CHAPTER II

PREPARATION AND CHARACTERIZATION OF TRANS-1,2-CYCLOPENTANEDIAMINE

Preparation of Starting Material

Starting material for the preparation of trans-1,2-cyclopentanediamine was adipic acid. Fisher esterification of the adipic acid yielded diethyladipate. Dieckmann ring closure of this ester produced 2-carbethoxycyclopentanone. Reaction of 2-carbethoxycyclopentanone with sodium nitrite in base followed by acidification with sulfuric acid and then addition of hydroxylamine yielded 1,2-cyclopentanedioxime. Reduction of the 1,2-cyclopentanedioxime with sodium in ethanol yielded 1,2-cyclopentanediamine.

Preparation of Diethyl Adipate

Diethyl adipate was prepared by Fisher esterification of adipic acid with ethanol. Five hundred g. of adipic acid was heated under reflux with two liters of absolute ethanol and two milliliters of concentrated sulfuric acid in a three-liter flask for twenty-four hours. The reaction mixture was cooled and 100 g. of sodium hydroxide dissolved in approximately 1500 ml. of water was added, causing two layers to separate. The entire mixture was extracted with three 500-ml. portions of diethyl ether. The water layer was saved for recovery of adipic acid and monoethyl adipate.

The ether extract was washed with 25 ml. of saturated sodium

chloride solution; the ether extract was then dried over anhydrous magnesium sulfate overnight. The magnesium sulfate was filtered off and washed with diethyl ether. The washings were combined with the ether extract and the ether and unreacted alcohol were distilled off at atmospheric pressure. The diethyl adipate was distilled at reduced pressure (130-138°/16 mm). The yield, based on the amount of adipic acid used, was about 85 per cent.

The unreacted adipic acid and monoethyl adipate were recovered by adding enough concentrated hydrochloric acid to the water extract to reduce the pH to one or two. Usually two layers separated at this point. The entire mixture was extracted with three 300-ml. portions of diethyl ether, the ether extract was washed with 25 ml. of saturated sodium chloride solution. The extract was then dried over anhydrous magnesium sulfate overnight.

The ether was distilled off at atmospheric pressure, then the monoethyl adipate was distilled under reduced pressure (125-135°/7 mm). Any unreacted acid remaining in the still pot was recrystallized once from ethanol and both the monoethyl adipate and the recovered adipic acid were reesterified.

Preparation of 2-Carbethoxycyclopentanone

The 2-carbethoxycyclopentanone was prepared by the method of Pinkey (16). Fifty g. of sodium, cut in small pieces, was added to a three-liter, one-neck, flask which contained 1,250 ml. of dry benzene. To this was added 303 g. of diethyl adipate and three ml. of absolute ethanol. The flask was fitted with a reflux condenser and heated for 24 hours. During the course of the reaction a white solid formed on the

surface of the sodium; this was broken up by vigorous shaking. After heating, the semi-solid reaction mixture was broken up by stirring and the mixture was cooled in an ice bath. The unreacted sodium was decomposed by slowly adding ice and concentrated hydrochloric acid, with vigorous stirring, until the methyl orange end point was reached. The water and benzene layers were separated and the water layer was extracted once with 300 ml. of fresh benzene. This benzene extract was combined with the original benzene layer and washed with 300 ml. of five per cent sodium carbonate solution followed by 300 ml. of distilled water and finally by 25 ml. of saturated sodium chloride solution. The benzene extract was then dried over anhydrous magnesium sulfate for 24 hours.

The magnesium sulfate was then filtered off and washed with 100 ml. of benzene. The washings were added to the extract and the benzene was distilled off at atmospheric pressure. The 2-carbethoxycyclopentanone was distilled off under reduced pressure (115-119°/16 mm.). The yield, based on the amount of diethyl adipate used, was 83 per cent.

Preparation of 1,2-Cyclopentanedioxime

The 1,2-cyclopentanedioxime was prepared by the method of Cope, et al., (17). A one-liter, three-neck, flask was equipped with a mechanical stirrer, a gas inlet tube, and a gas outlet. To the flask, 63 g. of 2-carbethoxycyclopentanone was added followed by 27.8 g. of sodium nitrite dissolved in 64 ml. of water. Then 17 g. of sodium hydroxide dissolved in 320 ml. of water, was added. Upon the addition of the sodium nitrite and sodium hydroxide a white precipitate formed. Nitrogen was passed over the mixture while it was stirred. Stirring was continued until all of the solid dissolved, usually 48 hours.

The mixture was then cooled to zero degrees in an ice-salt bath and 120 ml. of six normal sulfuric acid was slowly added, care being taken that the temperature did not arise above ten degrees. After the addition of the acid the yellow mixture was extracted as rapidly as possible with two 200-ml. portions of diethyl ether. The water layer was separated and continuously extracted for 36 hours with diethyl ether. During the continuous extraction the water layer turned black.

The ether extracts were combined and reduced to 100 ml. total volume. The extract was then cooled in an ice bath and an aqueous solution containing 27.8 g. of hydroxylamine hydrochloride and 16.0 g. of sodium hydroxide was slowly added. During the addition sufficient heat was generated to boil the ether and a brown to black precipitate of 1,2-cyclopentanedioxime formed. The mixture was stored overnight at ten degrees, filtered and the precipitate was washed once with fifty ml. of cold water. The resulting brown solid was then recrystallized by dissolving it in warm dilute sodium hydroxide solution, cooling and then adding one normal hydrochloric acid until precipitation occurred. The light tan precipitate was filtered and air dried. The yield, based on the amount of 1,2-carbethoxycyclopentanone used, was 73 per cent.

Reduction of 1,2-Cyclopentanedioxime with $LiAlH_4$

Twelve g. of 1,2-cyclopentanedioxime was placed in the cup of a Soxhlet extractor which was then placed on a 500-ml. flask. The flask contained 250 ml. of anhydrous tetrahydrofuran, eight g. of lithium aluminum hydride and was equipped with a heating mantel and magnetic stirrer. The mixture was then stirred and refluxed until all the dioxime had

dissolved, usually 24 hours. The mixture was then cooled and water was very slowly added, with stirring, until all of the excess lithium aluminum hydride had decomposed. The mixture was then filtered to remove the precipitated aluminum hydroxide and most of the lithium hydroxide. The excess tetrahydrofuran was then removed at atmospheric pressure and the residue was analyzed to determine the amount of amine formed. In all cases the yield of amine was quite low. The average yield for several runs was 15 per cent of the theoretical yield.

Reduction of 1,2-Cyclopentanedioxime with Sodium in Ethanol

The 1,2-cyclopentanedioxime was reduced by the method of Jaeger (5) and Cope (17). Ten g. of 1,2-cyclopentanedioxime and 600 ml. of absolute ethanol were added to a one-liter, three-neck flask equipped with a reflux condenser and a mechanical stirrer. To the stirred mixture 90 g. of sodium ribbon was added as rapidly as possible without distilling the ethanol out of the water cooled condenser. The solution turned dark brown and then yellow during the course of the reaction. After all the sodium had been added, the mixture was heated at reflux until all of the sodium had dissolved, usually four to six hours.

When the reaction was complete the resulting amine was isolated by two different methods. In the first method the reaction mixture was steam distilled until the bulk of the alcohol had distilled over. The remaining amine-water-sodium hydroxide mixture was cooled and then continuously extracted with diethyl ether for 48 hours. The ether was then distilled off at atmospheric pressure and the amine was fractionally distilled at reduced pressure through a spinning band column at a pressure

of ten millimeters and a reflux ratio of 35 to one. Typical distillation data are found in Table 1. The yield of pure amine was 30-35 per cent of theoretical. The second method used to isolate the amine was to take the mixture, after the sodium in ethanol reduction was complete, and steam distill it as rapidly as possible. The steam distillation was continued until all of the ethanol had been distilled and 1 to 1.5 liters of water-amine mixture had distilled over. The distillates were combined and concentrated hydrochloric acid was added until the solution had a pH of approximately one. The mixture was then evaporated on a rotary evaporator connected to a water aspirator. The resulting yellow to brown solid was washed twice with small portions of cold ethanol, filtered and dried in a vacuum desiccator. The yield of white, crystalline trans-1,2-cyclopentanediamine dihydrochloride was 60 to 70 per cent of theoretical.

Table 1. Distillation Data of Trans-1,2-Cyclopentanediamine.

Head Temperature	Pressure mm Hg	Sample Volume
55-56	10	2 ml.
56-58	10	2 ml.
58-59	10	45 ml.
59-	5	2 ml.

The infrared spectrum of the first fraction of distilled amine is almost identical with the spectrum of later fractions. The only significant difference is in the region of 6.2 microns. In the first fraction a

small peak of variable intensity occurs at 6.2 microns but is absent in the latter fractions. This peak is thought to be caused by ammonia which absorbs in this region (18) and is often present as a decomposition product of the amine. The infrared spectra of the aminedihydrochloride is the same as that of the amine obtained by distillation.

Preparation of trans-1,2-Cyclopentanediaminedihydrochloride from trans-1,2-Cyclopentanediamine

Approximately four ml. of distilled trans-1,2-cyclopentanediamine was added to 100 ml. of dry diethyl ether and then dry hydrogen chloride was passed through the solution for two hours. The white crystalline trans-1,2-cyclopentanediaminedihydrochloride was filtered by suction, washed with a few milliliters of cold absolute ethanol and air dried.

Attempted Stereospecific Preparation of Cis-1,2-Cyclopentanediamine

Attempts were made to stereospecifically prepare the other geometrical isomer, cis-1,2-cyclopentanediamine. The method attempted was the conversion of cis-1,2-cyclopentanedicarboxylic acid to the corresponding diamine by means of the Schmidt reaction. The cis-1,2-cyclopentanedicarboxylic acid was prepared by the method of Perkin (19) and by the method of Fuson (20).

Preparation of cis-1,2-Cyclopentanedicarboxylic Acid by the Method of Perkin

Preparation of Tetraethyl-1,1,5,5-pentane Tetracarboxylate

A one-liter, three-neck flask was equipped with a reflux condenser, efficient mechanical stirrer and a dropping funnel. Six hundred

milliliters of absolute ethanol was then added to the flask and then 23 g. of sodium metal, cut in small pieces, was added and the mixture was stirred until all of the sodium had dissolved. The entire mixture was then cooled in an ice bath and a mixture of 128 ml. of diethyl malonate and 52 ml. of 1,3-dibromopropane was slowly added, care being taken that the temperature did not rise above 30 degrees during the addition. The ice bath was then removed and the mixture was allowed to stand; a reaction soon set in and generally was accompanied by evolution of heat sufficient to cause the alcohol to boil. As soon as this had subsided and the whole cooled down again, the reaction was complete. Five hundred milliliters of water and sufficient concentrated sulfuric acid to make the mixture acidic were added and the entire mixture was extracted with two 500-ml. portions of diethyl ether. The ether was then distilled off at atmospheric pressure and the residue was rapidly steam distilled until no more oily drops came over with the water. This removed most of the unreacted starting materials. The remaining material in the distillation pot was extracted with 200 ml. of diethyl ether, the ether extract was washed with 25 ml. of five per cent sodium carbonate solution and then dried over calcium chloride. The ether was then distilled off at atmospheric pressure and the crude tetraethyl-1,1,5,5-pentanetetracarboxylate was used without further purification. The yield of crude product was 75 per cent of theoretical.

Preparation of trans-1,2-Cyclopentanedicarboxylic Acid

To a one-liter, three-neck flask equipped with a reflux condenser, mechanical stirrer, and dropping funnel, 100 ml. of dry methanol was added. Seventeen grams of sodium metal, cut in small pieces, was

was added and stirred until all the sodium had dissolved. Four hundred milliliters of dry ether was then added and then 135 g. of tetraethyl-1,1,5,5-pentanetetracarboxylate. The mixture was then stirred and cooled in an ice bath and 20 ml. of dry bromine was added. After the addition of the bromine, the reaction mixture was allowed to stand for approximately one hour, then an equal volume of water was added and the ether layer was separated.

The ether was removed by distillation at atmospheric pressure. Then a mixture of 90 g. of potassium hydroxide, 200 ml. of ethanol, and 50 ml. of water was added to the pot residue. The mixture was then refluxed overnight. The solvent was removed on a rotary evaporator attached to a water aspirator and the solid residue was dissolved in water, made strongly acidic with sulfuric acid, and continuously extracted with diethyl ether for 48 hours. The ether was removed by distillation at atmospheric pressure and the crude product was recrystallized from water.

The yields of trans-1,2-cyclopentanedicarboxylic acid were quite low. Therefore, the following method was used for the preparation of trans-diacid which was then converted to the cis-acid.

Preparation of cis-1,2-Cyclopentanedicarboxylic Acid by the Method of Fuson

Preparation of Ethyl-α,α'-Dibromopimelate

Forty-four grams of pimelic acid was placed in a 250-ml. flask and 85 ml. of thionyl chloride was added. The mixture was then refluxed for three hours. At the end of that time, the excess thionyl chloride was distilled off at reduced pressure. Twenty milliliters of chloroform

were added to the flask, stirred, and then the chloroform was distilled off at reduced pressure to remove the last traces of the unreacted thionyl chloride.

The resulting pimelyl chloride was brominated without further purification. To the pimelyl chloride 32 ml. of dry bromine were added over a period of six hours with continuous stirring. During the addition of the bromine the temperature was maintained at 80 degrees. The reaction mixture was allowed to stand overnight and then heated for an additional two hours. The mixture was then cooled in an ice bath and 200 ml. of ice cold absolute ethanol were slowly added with stirring and the resulting mixture was allowed to stand overnight. To the ethanolic mixture 200 ml. of water were added and the resulting two layers were separated. The aqueous layer was extracted with two 200-ml. portions of diethyl ether and the ether extract was added to the non-aqueous layer. The extract was then washed with 50 ml. of five per cent sodium sulfite, then with 100 ml. of ten per cent sodium carbonate, and finally with 100 ml. of water. The ether was removed by distillation at atmospheric pressure and the crude product was used without further purification. The yield of crude diethyl-α,α'-dibromopimelate was 90 per cent of theoretical.

Preparation of Ethyl-1-cyano-1,2-cyclopentanedicarboxylate

Ninety-one grams of diethyl-α,α'-dibromopimelate was placed in a 250-ml. round-bottom flask and 55 ml. of absolute ethanol and 46 g. of sodium cyanide were added. The mixture was then refluxed for 60 hours. The unreacted sodium cyanide and the sodium bromide that had formed were removed by filtration. The ethanol was distilled off at atmospheric pressure and the desired product was distilled at reduced pressure (140-

150°/4 mm). The reaction gave an 81 per cent yield of theoretical of light yellow oil.

Preparation of trans-1,2-Cyclopentanedicarboxylic Acid

Forty-eight grams of diethyl-1-cyano-1,2-cyclopentanedicarboxylate was added to 150 ml. of concentrated hydrochloric acid in a 300-ml. round-bottom flask. The mixture was then refluxed for 90 hours. At the end of that time, the solution was cooled in an ice bath and the trans-1,2-cyclopentanedicarboxylic acid precipitated. The mixture was filtered and the white crystalline acid was washed once with a few milliliters of ice cold water. The yield was 80 per cent of theoretical.

Conversion of trans-1,2-Cyclopentanedicarboxylic Acid to cis-1,2-Cyclopentanedicarboxylic Acid

The trans-1,2-cyclopentanedicarboxylic acid from both methods of preparation was converted to the cis-1,2-cyclopentanedicarboxylic anhydride and then to cis-1,2-cyclopentane dicarboxylic acid in the following manner.

Twenty grams of trans-1,2-cyclopentanedicarboxylic acid was placed in a 300-ml., round-bottom flask with 150 ml. of acetic anhydride and refluxed overnight. During the reflux the reaction mixture turned black. The acetic anhydride was removed by distillation at atmospheric pressure and the remaining crude cis-anhydride was refluxed overnight with 100 ml. of 20 per cent potassium hydroxide solution. The reaction mixture was then acidified with concentrated hydrochloric acid and cooled in an ice bath. The resulting white crystals were separated by filtration and washed once with a few milliliters of ice cold water. The yield of cis-1,2-cyclopentanedicarboxylic acid was 35 per cent of theoretical.

Attempted Preparation of cis-1,2-Cyclopentanediamine

The cis-1,2-cyclopentanedicarboxylic acid was used as the starting material for the stereospecific Schmidt reaction (21), which converts the acid directly to the corresponding amine. Two different modifications of the reaction were attempted as follows:

Seven grams of cis-1,2-cyclopentanedicarboxylic acid was placed in a 250-ml., three-neck flask equipped with a mechanical stirrer and a reflux condenser. Fifty milliliters of chloroform and 30 ml. of concentrated sulfuric acid were added to the flask and then seven grams of sodium azide was added in small portions. During the addition of the sodium azide, the temperature was kept between 40 and 45 degrees. After all the sodium azide had been added, the mixture was stirred and heated until no more gas evolution could be observed, usually 24 hours. The mixture was then cooled and poured over 100 grams of cracked ice. The aqueous layer was separated from the chloroform layer.

Seventy-five grams of potassium hydroxide were dissolved in 100 ml. of water and slowly added to the aqueous layer. The aqueous layer was then continuously extracted with diethyl ether for 24 hours. The ether was then distilled off at atmospheric presure and the residue was dissolved in absolute ethanol. The ethanolic solution was acidified with concentrated hydrochloric acid and evaporated to dryness. The small amount of white crystalline solid which remained was assumed to be the desired cis-1,2-cyclopentanediaminedihydrochloride.

On repeating the above reaction a second time, no isolatable product was formed.

A second modification of the Schmidt reaction was then attempted.

Nine grams of cis-1,2-cyclopentanedicarboxylic acid was placed in a three-neck, 300-ml. flask, equipped with a mechanical stirrer, reflux condenser, and a dropping funnel. Twenty milliliters of concentrated sulfuric acid was added to the flask and then a solution of hydrazoic acid in chloroform (approximately 150 ml. of 0.10 M hydrazoic acid) was added at a rate to keep the temperature at approximately 50 degrees. A large amount of gas was evolved during the addition of the hydrazoic acid solution. As soon as the evolution of gas ceased, the solution was cooled and extracted with three 200-ml. portions of water. The water extract was made strongly alkaline with potassium hydroxide and was extracted overnight with diethyl ether. The ether was distilled off at atmospheric pressure. No residue remained in the distillation pot which should have contained any product that had been formed.

Attempted Chromatographic Separation of cis- and trans-1,2-Cyclopentanediamine

Since Phillips and Royer (15) had reported the separation of a small amount of cis-diamine from the trans-diamine by fractional distillation it was decided to attempt a chromatographic separation of the two geometrical isomers based on the separation of various diamines reported by Latterell and Walton (22).

Dowex 50W-X4 cation-exchange resin was stirred in a solution of nickel(II) chloride and concentrated ammonium hydroxide until the resin had been converted to the nickel-ammonia complex form. The resin was then placed in a column (3 x 45 centimeters) and washed with water until the pH of the effluent was approximately seven.

Five milliliters of freshly prepared 1,2-cyclopentanediamine,

made by the reduction of the dioxime with sodium in ethanol, was added to the top of the column. (The column turned from bluish-green to purple when the amine was added.) The amine was then eluted, with dilute ammonia solution; the concentration of ammonia was increased from 0.75 to 1.00 molar.

Evaporation of the collected fractions and inspection of the infrared spectrum of each residue showed that the amine was completely eluted by one molar ammonia solution and that there was no detectable separation of the amine into its two geometrical isomers.

CHAPTER III

PREPARATION OF COBALT(III) COMPLEXES

Sodium triscarbonatocobaltate(III) trihydrate was prepared by hydrogen peroxide oxidation of cobalt(II) nitrate hexahydrate in the presence of sodium bicarbonate. The cyclopentanediamine complexes were then prepared by adding 1,2-cyclopentanediamine dihydrochloride to a slurry of the sodium triscarbonatocobaltate(III) trihydrate.

Preparation of Sodium Triscarbonatocobaltate(III) Trihydrate

The sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bauer and Dinkard (23). Twenty-five milliliters of water was added to a 250-ml. beaker containing 23 g. of sodium bicarbonate. The beaker was immersed in an ice bath and the mixture was stirred with a magnetic stirrer.

A mixture of 14.6 g. of cobalt(II) nitrate hexahydrate and 10 ml. of 30 per cent hydrogen peroxide was dissolved in 25 ml. of water. The cobalt(II) hydrogen peroxide solution was then slowly added to the sodium bicarbonate water mixture. During the addition of the cobalt(II) solution the temperature was not allowed to rise above five degrees. The mixture effervesced quite vigorously and turned green. Stirring was continued after the cobalt(II) solution was added until effervescence had ceased, approximately 30 minutes.

The green precipitate which formed was filtered by suction, washed thoroughly with water three times, followed by two washings with absolute

alcohol to remove any unreacted cobalt(II) and then with diethyl ether. The yield of light green powder was 38 per cent of theoretical. The green filtrate doubtlessly contains much more product but no effort was made to recover it.

The sodium triscarbonatocobaltate(III) trihydrate was prepared as needed, as it slowly decomposed on standing and has a useful shelf life of about two weeks.

Preparation of 1,2-Cyclopentanediamine Cobalt(III) Complexes

Attempted Preparation of tris- cis-1,2-Cyclopentanediamine Cobalt(III) Chloride

A slurry of 0.60 g. of sodium triscarbonatocobaltate(III) trihydrate and one ml. of water was warmed on a water bath. One gram of cis-1,2-cyclopentanediamine dihydrochloride was added to the slurry. The amine dihydrochloride was derived from the amination of the cis-1,2-cyclopentanedicarboxylic acid (see page 18). Frothing occurred immediately and the slurry was heated on a water bath for 15 minutes. After effervescence had ceased, five milliliters of absolute ethanol was added to the dark colored colusion. Filtration yielded a bright green residue and a purple filtrate.

These compounds were not analyzed due to the small amount of material available but the colors are analogous to the trans-bisethylenediaminedichlorocobalt(III) chloride (green) and the cis-bis-ethylenediaminedichlorocobalt(III) chloride. Royer and Phillips (15) also observed the formation of a green compound and a purple compound in the reaction of 1,2-cyclopentanediamine dihydrochloride with sodium tris-carbonatocobalt

(III) trihydrate.

In an attempt to recover the amine in the complexes, the residue and the filtrate were dissolved in water and the solution was made strongly aklaine. The solution was then continuously extracted with diethyl ether for 24 hours. The ether was distilled off at atmospheric pressure but there was insufficient amine to allow any characterization to be carried out.

Preparation of $[Co(cptdin)_3(CO_3)(H_2O)]Cl$

To a slurry of seven grams (.019 mole) of sodium tris-carbonatocobaltate(III) trihydrate 11.6 g. (.066 mole) of racemic trans-1,2-cyclopentanediamine dihydrochloride was added and the mixture was warmed, with stirring, on a water bath. Considerable frothing occurred with the original green mixture turning black, then brown, and finally deep reddish brown. The cptdin·2HCl used in this preparation and all the following preparations was prepared by reduction of 1,2-cyclopentanedioxime with sodium in ethanol.

The red mixture was cooled and several milliliters of absolute ethanol was added to precipitate the complex. The complex was filtered by suction and washed several times with absolute ethanol to remove any cobalt(II) and excess amine or amine decomposition products that were present. The residue was then washed with diethyl ether and dried.

The reddish brown solid was then dissolved in water and filtered to remove any unreacted tris-carbonatocobaltate(III) trihydrate and any water insoluble reaction products.

The preparation was repeated numerous times with the amine to cobalt ratio varied from 3.5:1 up to 4:1. In each case the results were

the same. The yields of the desired product were low and there was always some pink $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ formed.

Methods of Analysis

Ionic chloride was determined by potentiometric titration of an aqueous solution of the complex using silver and calomel electrodes and employing a potassium nitrate agar-agar salt bridge. Approximately 0.02 g. of the complex was dissolved in 10 ml. of water and titrated with silver nitrate solution using a micro-buret.

Because the covalent chloride is strongly bound to the cobalt(III) in complexes, the covalent chloride can be determined only by destroying the complex. Approximately 0.02 g. of the complex was dissolved in 2 ml. of water and approximately 0.05 g. of potassium hydroxide was added. The solution was heated to dryness, cooled and the black residue taken up with 2 ml. of perchloric acid. The solution was diluted to 10 ml. with water and titrated with silver nitrate solution. The chloride thus determined was the ionic chloride plus the covalent chloride. The covalent chloride was determined by subtracting the ionic chloride from the total chloride.

The silver nitrate solution used was prepared from reagent grade silver nitrate. The solution was standardized by potentiometric titration of a solution prepared from reagent grade potassium chloride which had been dried at 120 degrees for 24 hours. The silver nitrate solution was stored in a dark bottle and was restandardized frequently.

Cobalt was determined by titration with ethylenediaminetetraacetic acid (EDTA) using murexide as the indicator. Approximately 0.02 g. of the complex was dissolved in 2 ml. of water and approximately 0.02

g. of potassium hydroxide was added. The solution was warmed and then evaporated to a small volume. After cooling, the black residue was taken up in a minimum amount (approximately 0.5 ml.) of concentrated hydrochloric acid. The solution was then evaporated almost to dryness to expel the excess acid and then neutralized with concentrated ammonium hydroxide. Approximately 15 ml. of water was added and then 5 ml. of pH 10 buffer was added. A small amount of solid murexide indicator was added and the solution was then titrated with a solution of EDTA using a micro-buret. The color change at the end point was from yellow to violet.

The EDTA was standardized against a solution of copper(II) nitrate. Copper metal was weighed into a beaker and dissolved in concentrated nitric acid. The excess acid was boiled off and the solution was transferred to a volumetric flask and diluted to the mark. An aliquot of the copper solution was placed in a beaker; an approximately equal volume of ethanol was added, followed by an equal volume of pH 5 buffer. A few drops of 1-(2-pyridylaza)-2-naphthol (PAN) dissolved in ethanol were added and the solution was titrated with EDTA. The color change at the end point was from violet to yellowish green.

The EDTA solution, the buffer solutions and the standard copper (II) nitrate solution were all stored in polyethylene bottles and the EDTA solution was restandardized from time to time.

The buffers were prepared from ammonium chloride and ammonium hydroxide in the case of the pH 10 buffer and from sodium acetate and acetic acid in the case of the pH 5 buffer.

Coordinated carbonate was determined by adding approximately 0.02

g. of the complex to concentrated sulfuric acid in a special system (Figure 1) and trapping the evolved carbon dioxide in a previously weighed tube containing ascarite (sodium hydroxide on an asbestos support) and determining the change in weight of the ascarite absorption tube.

Carbon, hydrogen, and nitrogen analyses were made by Galbraith Laboratories, Inc., of Knoxville, Tennessee.

Instrumentation Used

Infrared spectra were obtained by a mull technique. The complexes were first ground in an agate mortar with nujol or hexachlorobutadiene. The mulled material was then placed between sodium chloride plates and the spectrum was recorded on a Perkin-Elmer Infracord Model Spectrophotometer.

Visible spectra were obtained on either an Applied Physics Corp. Cary Model 14 or on a Bausch and Lomb Spectronic 505 recording spectrophotometer.

Molecular weights were determined by use of a Mechrolab Model 310 Vapor Pressure Osmometer.

Optical rotatory dispersion curves of the complexes were obtained by using a Perkin-Elmer Optical Rotatory Dispersion Accessory, Model 262-0448, in conjunction with the Cary Model 14 spectrophotometer.

Optical rotations of the free amine and the complex at a fixed wavelength of 540 millimicrons were obtained on a Bendix ETL-NPL Automatic Recording Polarimeter, Type 143 A.

Analytical weighings were done on either an Ainsworth Type 12

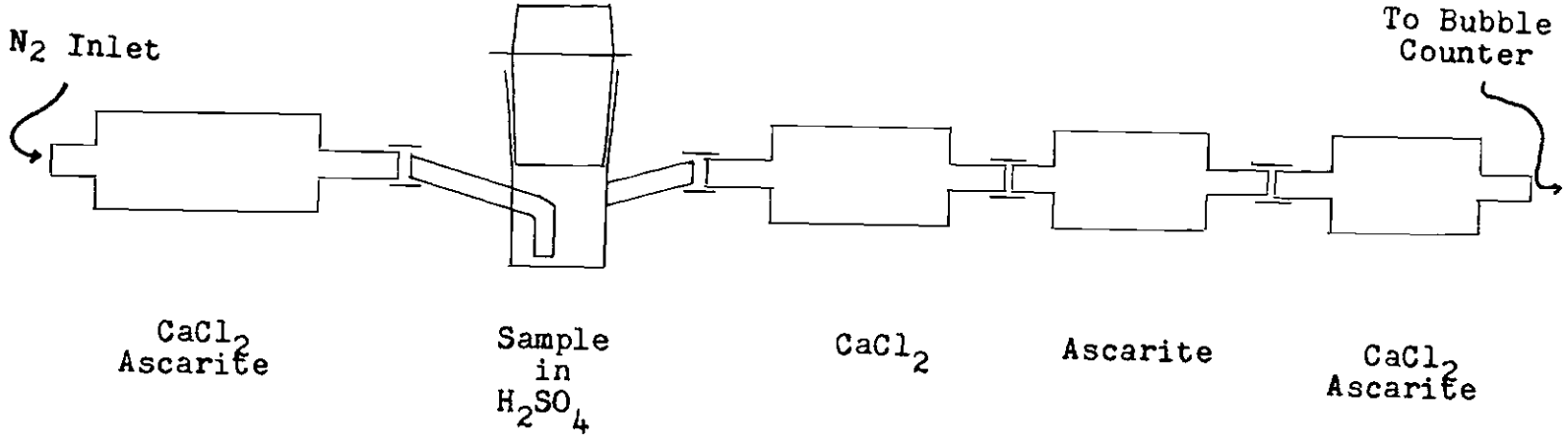


Figure 1. Apparatus For The Determination Of Coordinated Carbonate

single pan balance or on a Mettler Type H6 single pan balance.

Potentiometric and pH titrations were performed using a Beckman Zeromatic II pH meter and a Micro-Metric Instrument Co. Syringe Micro Buret Model No. SB2 equipped with syringes capable of delivering volumes of 0.50, 1.00, or 5.00 microliters.

Countercurrent distribution separations were performed using a two hundred transfer H. O. Post Scientific Co. Model B-3 Automatic Counter Current Distribution apparatus or a ten transfer H. O. Post Scientific Co. manually operated counter current distribution apparatus.

Fractional distillations of the amine were carried out using a laboratory size Nester-Faust Model NF-135 spinning band distillation column equipped with a stainless steel spinning band.

CHAPTER IV

CHARACTERIZATION OF $[Co(cptdin)_3(CO_3)(H_2O)]Cl$

Attempted Purification by Fractional Crystallization

A two-gram sample of the crude product from the reaction of racemic trans-1,2-cyclopentanediaminedihydrochloride with tris-carbonatocobaltate(III) chloride was dissolved in water and then the resulting solution was subjected to fractional crystallization. A small amount of the pink $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ was separated but the bulk of the material showed no effective separation after twelve cycles of fractional crystallization.

Attempted Purification by Ion Exchange Chromatography

An ion-exchange column 3 x 50 cm. was made up using Amberlite CG-50 400-600 mesh ion-exchange resin. A sample of the impure material from the attempted fractional crystallization was added to the top of the column and then dilute hydrochloric acid solutions were used in an attempt to elute the complex. The pH of the eluting solution was slowly decreased from 4.00 to 2.00. At a pH of 2.70 a pink solution was eluted from the column; this solution turned blue upon evaporation, indicating the presence of cobalt(II). Upon decreasing the pH of the eluting solution to 2.00 decomposition of the complex occurred.

A column similar to the one above was prepared, and an attempt was made to elute the complex by using solutions of calcium chloride of varying concentrations. However, the complex could not be eluted by solutions

containing concentrations of calcium ion up to two molar.

Separation of $[Co(cptdin)_3(CO_3)(H_2O)]Cl$ by Countercurrent Distribution

The solvent system for the countercurrent distribution separation was prepared by mixing water, n-butanol, and ethanol in the ratio of 10:10:1 by volume. The mixture was stirred overnight and then allowed to separate into two layers; the upper layer consisting of primarily n-butanol, and the lower layer consisting of primarily water.

A two-gram sample of the crude product obtained from the reaction of trans-1,2-cyclopentanediamine with tris-carbonatocobaltate(III) trihydrate was dissolved in approximately 50 ml. of the water layer. This solution was then placed in the first four tubes of a 200-transfer countercurrent distribution apparatus which contained the solvent described above. As the complex was transferred through the apparatus the impurities which were left behind caused emulsification of the two phases. As the trailing tubes became emulsified they were emptied and replaced by fresh lower phase.

The emulsified solvent mixture was evaporated at room temperature on a rotary evaporator attached to a water aspirator. The resulting residue was dissolved in water and the visible spectrum was obtained. The spectrum showed no maxima in the visible region which indicated that there was neither cobalt(II) nor cobalt(III) present in these fractions.

The apparatus was allowed to operate for approximately six weeks at which time the complex, due to the very low distribution coefficient, had only been transferred through the first 150 tubes of the apparatus.

The tubes were individually drained and the solvent was evaporated at approximately 60 degrees on a rotary evaporator attached to a

water aspirator. The resulting residue from each tube was then weighed, dissolved in a known amount of water, and the visible spectrum of the fraction was obtained.

The leading fractions of solvent yielded, upon evaporation, a reddish brown solid which was not identified. The middle fractions all contained a bright maroon material which was the desired complex. The trailing fractions show relatively large amounts of sodium chloride and varying amounts of the pink $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ complex. In some instances the trailing fractions also showed small, variable, amounts of purplish colored solid.

The visible spectra obtained from the middle fractions containing the maroon material were all very similar, having two maxima in the visible region. The only significant difference was in the ratio of the intensities (Figure 2) of the two maxima in the visible region.

In subsequent purifications of the complex, the method used was a modification of that just described. The solvent system was just n-butanol and water. The ten transfer, manually operated, countercurrent distribution apparatus was employed in place of the automatically operated unit. Although the purification with the manually operated apparatus was not as complete, its larger capacity (50 ml. of lower phase versus 10 ml. of lower phase) made the separation of large amounts of material much more rapid.

Resolution of the $[Co(cptdin)_3(CO_3)(H_2O)]Cl$

The material from the countercurrent distribution apparatus was converted from the chloride salt to the d-tartrate salt by stirring a

solution of the chloride salt with the calculated amount of silver-d-tartrate to cause precipitation of all the chloride as silver chloride. The solution was filtered to remove the precipitated silver chloride and any excess silver-d-tartrate. The resulting solution was then subjected to nine cycles of fractional crystallization.

At intervals, fractions were dissolved for the purpose of determining the specific rotation. The rotation and concentration of each solution were measured, using respectively the Bendix Automatic Polarimeter and the Cary 14 spectrophotometer. From the data obtained it appeared that there were two different complexes which were resolving to give a total of four different isomers. When the specific rotation of each fraction showed very little or no further change, the complexes were converted back to the chloride salt by passing each individual fraction through a 3 x 40 cm. ion-exchange column, which contained Dowex 1-X4 40-60 mesh resin in the chloride form. Each fraction was passed through the ion-exchange column twice. Between passages of the complex through the column the resin was washed with saturated sodium chloride solution and then with water until the effluent showed no further traces of chloride ion or sodium ion.

The rotations of the chloride salts were then determined and the salts were subjected to fractional crystallization until there was no further change in the specific rotations. This required four cycles of fractional crystallization.

In this manner a total of four fractions were obtained which showed different specific rotations: a very small amount of relatively insoluble material which had a high specific rotation and which will be called

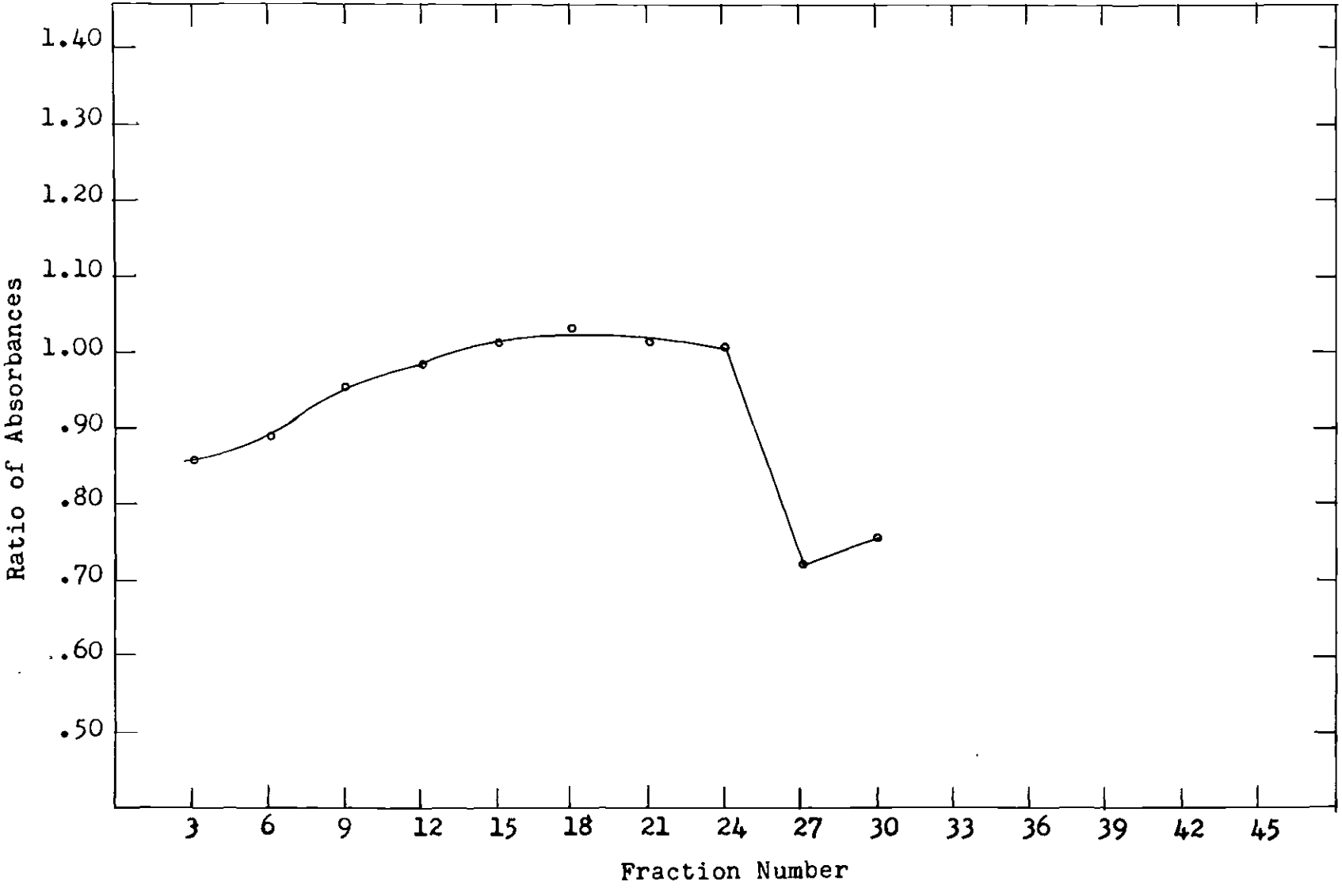


Figure 2. Counter Current Separation Of $[Co(cptdin)_3(CO_3)(H_2O)]Cl$

fraction one; two fractions of intermediate solubility which showed specific rotations of approximately the same value but opposite in sign, these will be referred to as fraction two for the less soluble of the two and fraction three for the more soluble; and another fraction, hereafter called fraction four, which had a relatively high rotation but which was different in appearance from the other three fractions. Since fraction four was the most soluble fraction, it undoubtedly contained a mixture of several different materials.

Characterization of the Resolved Complexes

Most Insoluble High Rotation Fraction (Fraction One)

The most insoluble fraction was too small to characterize completely. The material showed two maxima in the visible spectrum, (Figure 3), one at 370 millimicrons and a second at 530 millimicrons. The long wavelength maxima is slightly more intense than the one at shorter wavelengths. The optical rotatory dispersion curve (Figure 4) shows a Cotton effect associated with the 530 millimicron maxima in the visible spectra. The calculated specific rotation of the complex was 2400 degrees at 540 millimicrons. The apparent molecular weight, determined by vapor pressure osmometry was 290. There was insufficient material to run complete elemental analysis. From the analytical data available, the material is thought to be a dimer with an approximate formula of $[Co_2(cptdin)_6(CO_3)_2]Cl_2$.

Analytical data gave the following result calculated for $[Co_2(cptdin)_6(CO_3)_2]Cl_2$; Co, 12.95%; Carbonate as CO_2, 9.67%; ionic chloride, 7.79%. Found: Co, 11.8%; Carbonate as CO_2, 8.65%; ionic chloride, 7.72%.

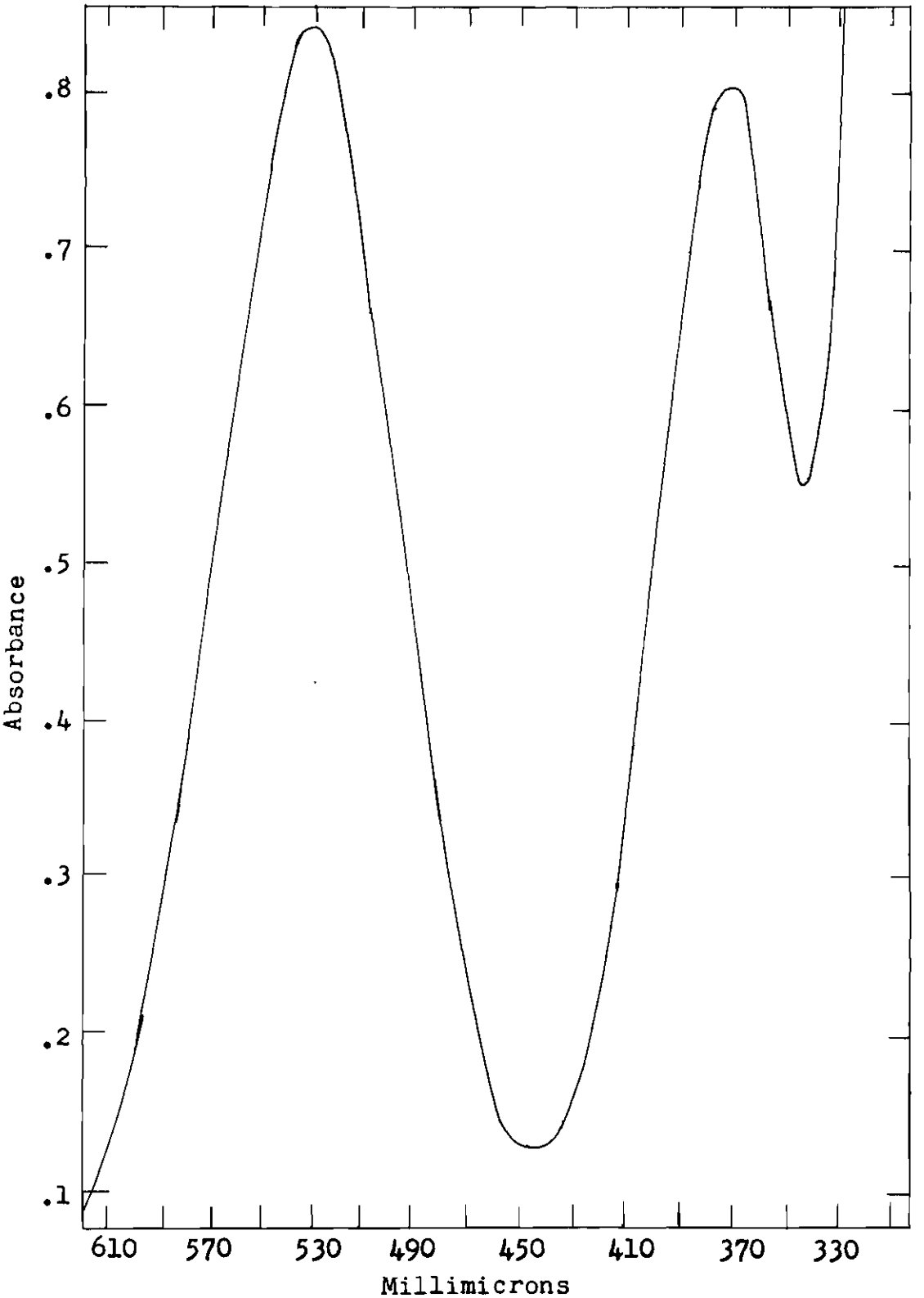


Figure 3. Visible Spectrum of $[Co_2(cptdin)_6(CO_3)_2]Cl_2$

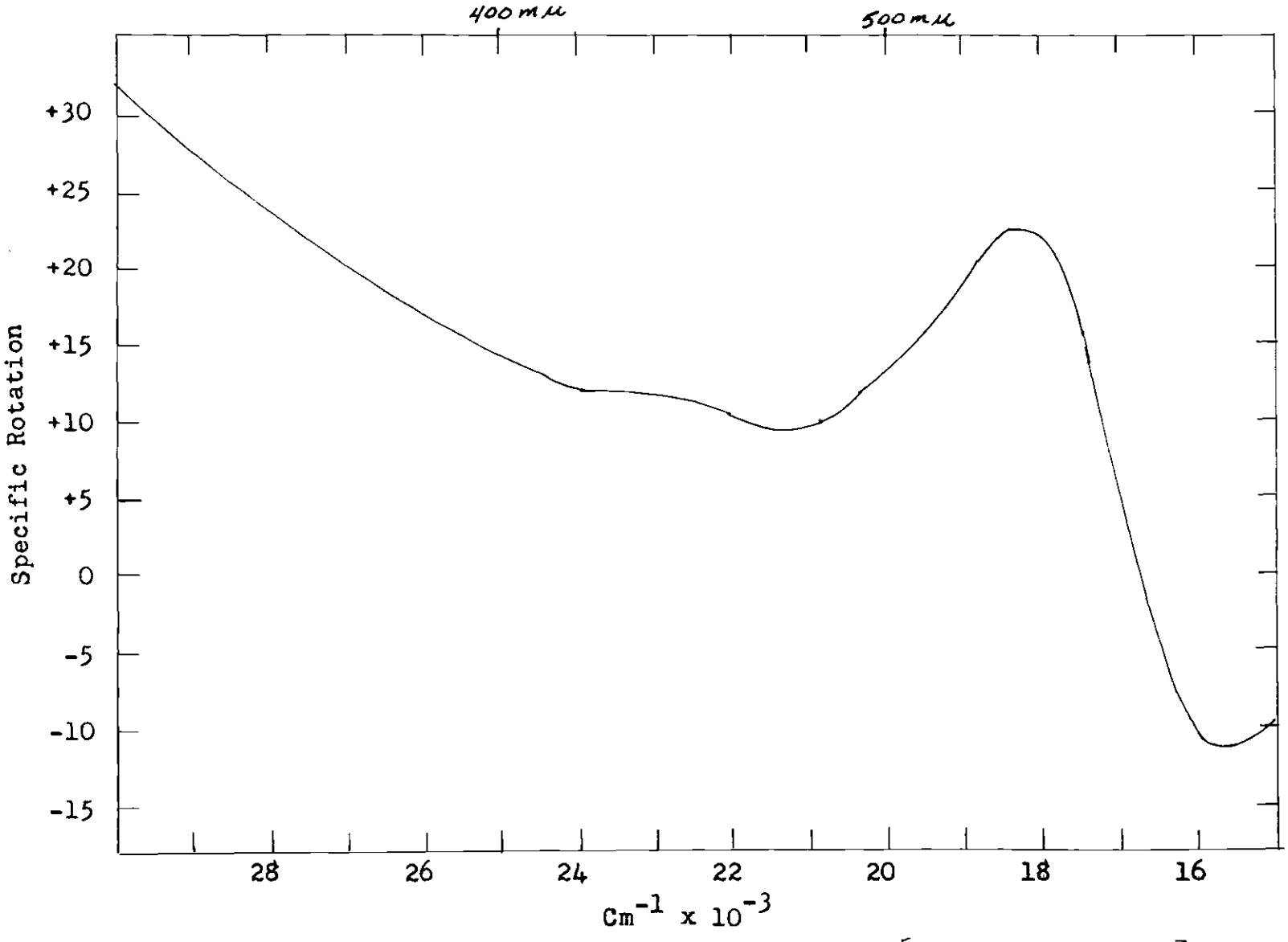


Figure 4. Optical Rotatory Dispersion Spectrum of $[Co_2(cptdin)_6(CO_3)_2]Cl_2$

Investigation of the infrared spectra (Figure 5) shows peaks at 1280 cm^{-1} which, according to Nakamoto (18), are characteristic of a bidentate carbonate group. However, there doesn't appear to be any absorption which could be attributed to a coordinated water molecule.

The apparent molecular weight for the dimeric formula is 303, assuming a 1:2 electrolyte, which agrees with the experimentally determined apparent molecular weight of 290. The presence of a polynuclear species is also supported by the optical rotatory dispersion curve which is similar to the optical rotatory dispersion curve of the binuclear $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ specie. There was insufficient material to allow a determination of the stereospecificity of the amines in the complex or to determine the difference, if any, in the manner in which the amines were coordinated.

Insoluble Low Rotation Fraction (Fraction Two)

The visible spectrum (Figure 6) of this fraction was almost identical to that of fraction one, however, the optical rotatory dispersion curve (Figure 7) was entirely different. In this case, there is no detectable Cotton effect anywhere in the visible region of the spectrum. The observed specific rotation of the complex was +31 $\pm$ 2 degrees at 540 millimicrons. Analytical data gave the following results: calculated for $[Co(cptdin)_3(CO_3)(H_2O)]Cl$; C, 38.1%; N, 17.8%; H, 8.10%; Co, 12.4%; ionic chloride, 7.50%; covalent chloride, none. Found: C, 37.42%; N, 15.47%; H, 7.10%; Co, 12.4%; ionic chloride, 8.10%; covalent chloride, none.

Although the per cent cobalt and chloride in the compound indicate a one to one ratio of these elements, it was desired to determine

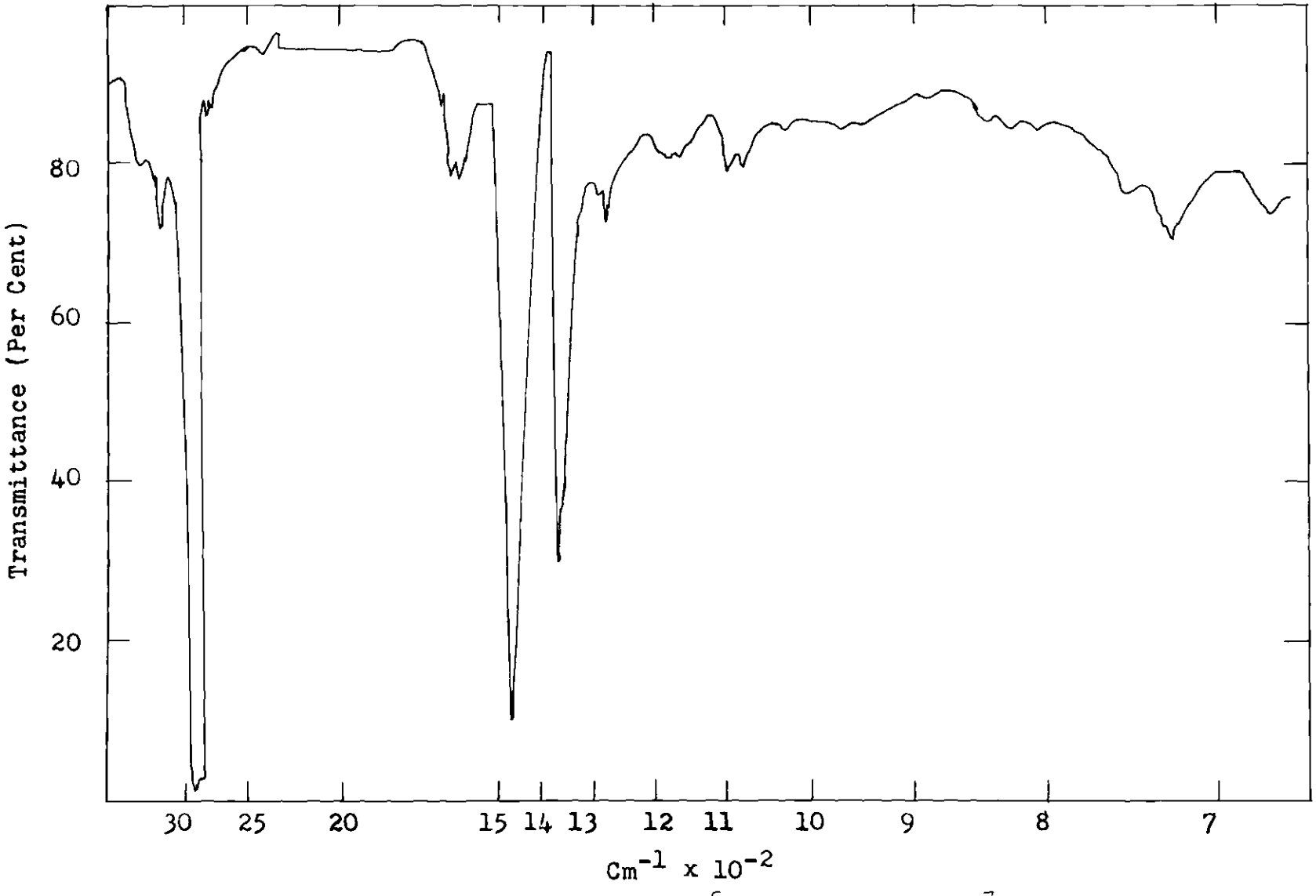


Figure 5. Infrared Spectrum of $[Co_2(cptdin)_6(CO_3)_2]Cl_2$

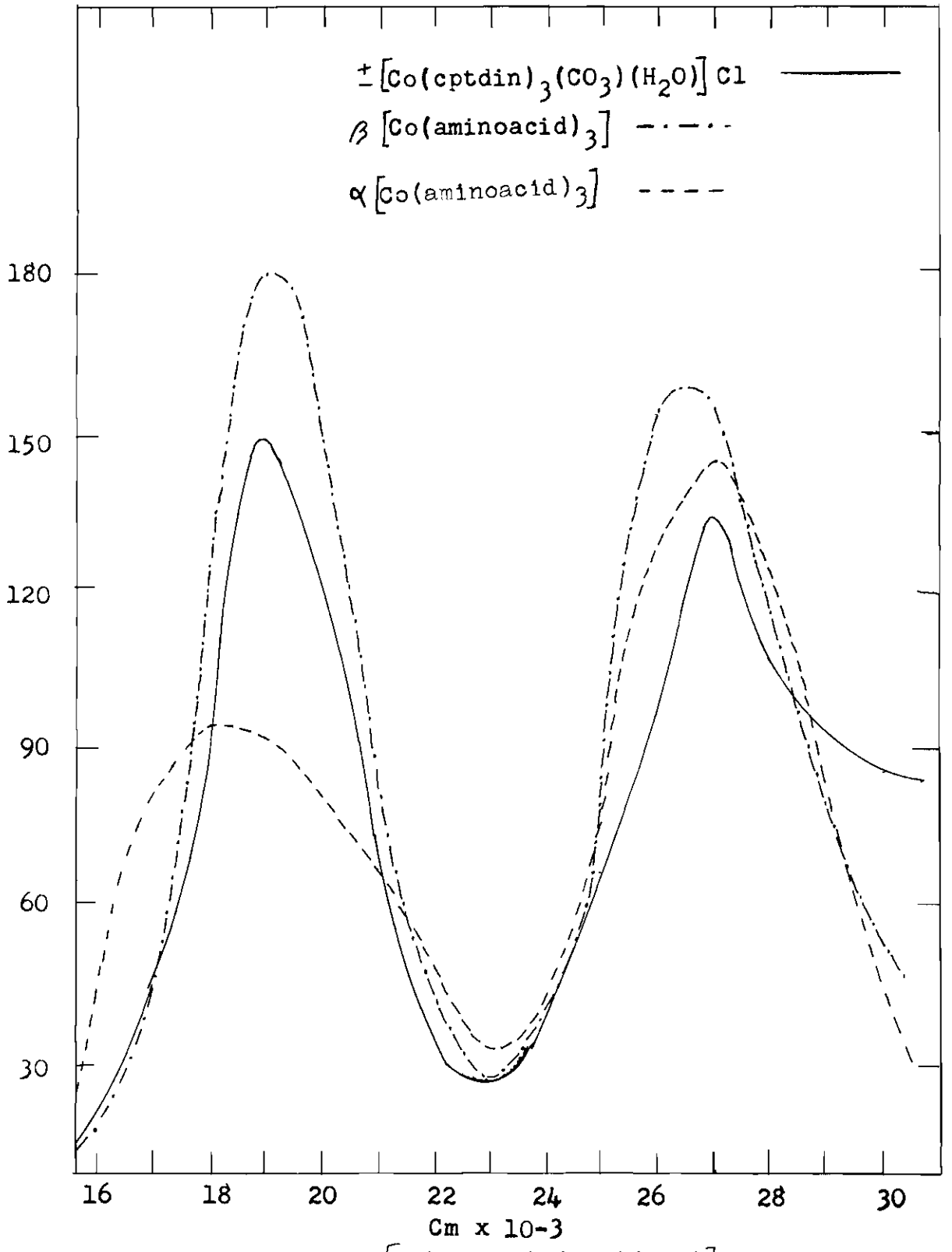


Figure 6. Visible Spectra of $[Co(cptdin)_3(CO_3)(H_2O)]Cl$ and the α and β Isomers of the Tris-Aminoacid Cobalt(III) Complexes

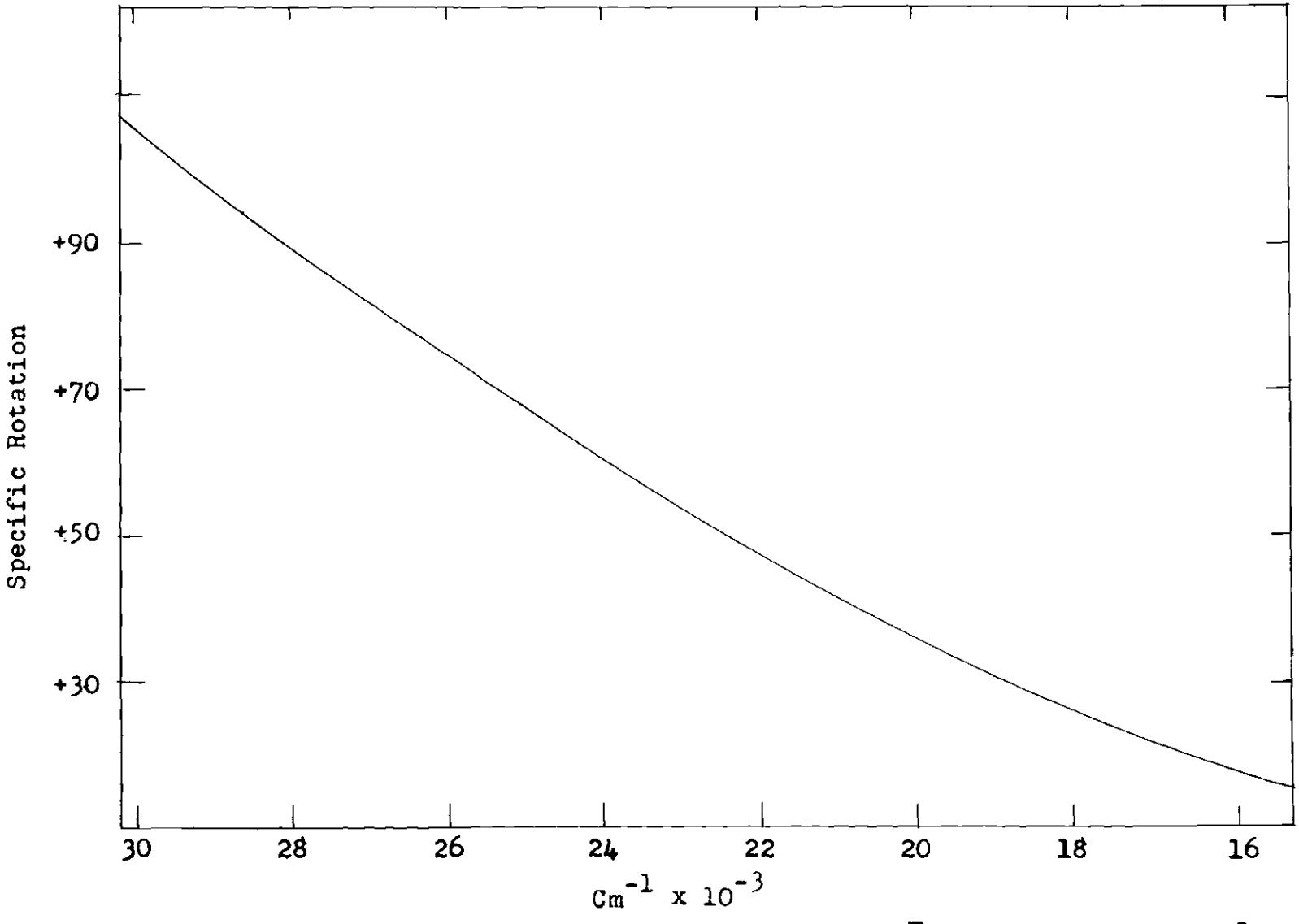


Figure 7. Optical Rotatory Dispersion Spectrum of $+[Co(cptdin)_3(CO_3)(H_2O)]Cl$

that there was only one carbonate ion per cobalt atom in the compound, and whether the carbonate was functioning as a monodentate ligand or as a bidentate ligand.

A weighed sample of the complex was placed in the specially constructed apparatus (Figure 1) containing concentrated sulfuric acid and the evolved carbon dioxide was swept out of the decomposition chamber and into the ascarite tube with a stream of dry, carbon dioxide free, nitrogen. In a typical run it was found that the complex contained 9.22 per cent carbon dioxide by weight. The per cent carbon dioxide calculated from the formula $[Co(cptdin)_3(CO_3)(H_2O)]$ Cl is 9.31 per cent.

An investigation of the infrared spectrum was made in order to determine if the carbonate was present as a monodentate ligand or as a bidentate ligand. A sample of the complex was first dissolved in deuterium oxide and allowed to stand for 48 hours. At the end of that time the D_2O, the H_2O, and HOD which had been formed were evaporated in a vacuum desiccator over sulfuric acid and the resulting solid was ground with nujol and the infrared spectrum of the sample was obtained (Figure 8). Another fraction of the solid was ground with hexachlorobutadiene and the infrared spectrum was again obtained. With the exception of the peaks from the solvent, the two spectra were identical. Inspection of the two spectra show peaks which are characteristic of those of a bidentate coordinated carbonate group. These occur at 1600 cm^{-1} and 1280 cm^{-1}. Investigation of the infrared spectra also shows an absorption peak, which may be attributed to a coordinated water molecule in the 900 cm^{-1} region.

In order to determine whether or not the complex was a monomer,

dimer, or some other polymeric species, it was necessary to determine the molecular weight of the material since the composition of the polymeric species are very similar to that of the monomer. The apparent molecular weight was determined by use of a vapor pressure osmometer. It was felt that this method was applicable due to the relatively high solubility of the complex, the relatively low charge on the cation, and the fact that the difference in apparent molecular weights of the monomer and dimer would be quite large.

The osmometer was operated using water as a solvent and an equilibrium temperature of 37 degrees. Standard solutions used to construct a known curve for comparison purposes were prepared from barium chloride dihydrate (a 1:2 electrolyte) and potassium chloride (a 1:1 electrolyte). Both standards gave superimposable curves at low concentrations and the complex gave a value of 229 for the apparent molecular weight. Assuming a one to one electrolyte, the calculated molecular weight for the monomer is 473 which would correspond to an apparent molecular weight of 236.

The specific rotation of the amine contained in the complex was determined by taking a weighed sample of the complex, dissolving it in two milliliters of water and adding approximately one milliliter of 0.10 molar potassium hydroxide. The resulting solution was warmed on a water bath at 60 degrees for approximately 30 minutes. The resulting cobalt oxide was filtered off, and the solution was transferred to a ten milliliter volumetric flask and diluted to the mark. The optical rotation was then determined using the Bendix Automatic polarimeter. The concentration of the amine in the solution was determined by titrating a portion of the amine solution with tenth normal hydrochloric acid and

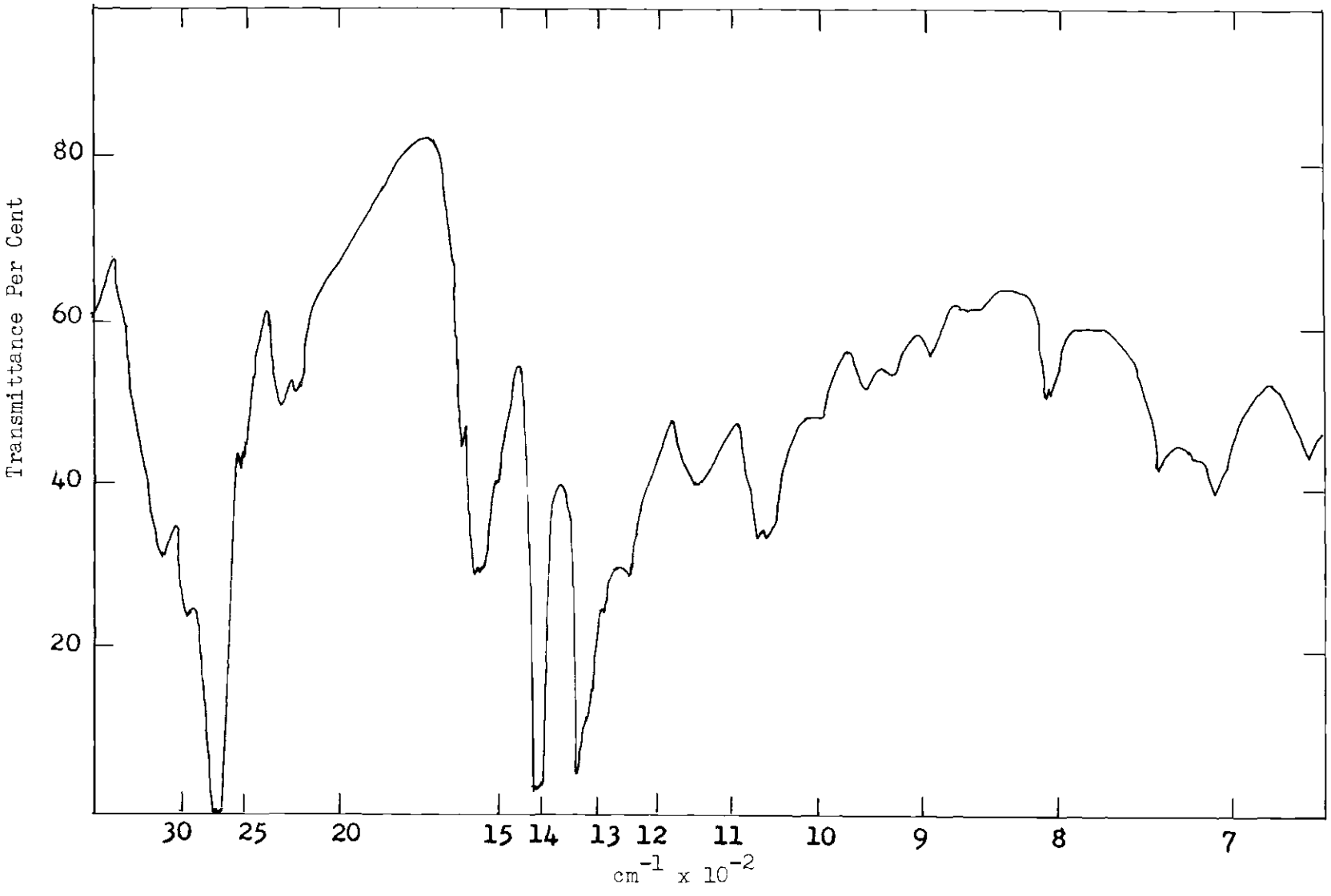


Figure 8. Infrared Spectrum of $[Co(cptdin)_3(CO_3)(H_2O)]Cl$

determining the end point with a pH meter. The specific rotation of the amine recovered from fraction two was +42.3 ± 2.0 degrees at 540 millimicrons.

This value of the rotation is in agreement with that of the optically pure amine as reported by Jaeger and Blumendal (5) and by Royer and Phillips (15). Jaeger reports a rotation of 35 degrees in water at the sodium D line and Royer reports a rotation of 42 degrees in benzene and 39 degrees in water at the sodium D line.

This agreement indicates that all of the amine molecules in the complex are of the same configuration. Otherwise the observed specific rotation would be much lower.

Characterization of the More Soluble Low Rotation Isomer (Fraction Three)

The more soluble low rotation complex was treated in the same manner as fraction two and gave substantially the same results. The visible spectrum is almost identical to that of fraction two, the only difference being in the ratio of the intensities of the two maxima. In the more soluble isomer the short wavelength maxima is slightly more intense than the long wavelength maxima. This can be attributed to contamination of this fraction by some soluble impurities from the more soluble fraction which shows an even greater difference in the ratio of the maxima in the visible spectra. The optical rotatory dispersion curve (Figure 9) is the mirror image of that of fraction two. The curve shows no Cotton effect in the visible region of the spectrum. The observed specific rotation of the complex is -29.9 ± 2.0 degrees at 540 millimicrons. The specific rotation of the recovered amine from the complex had a value of -38.7 ± 1.5 degrees at 540 millimicrons, again indicating that all the

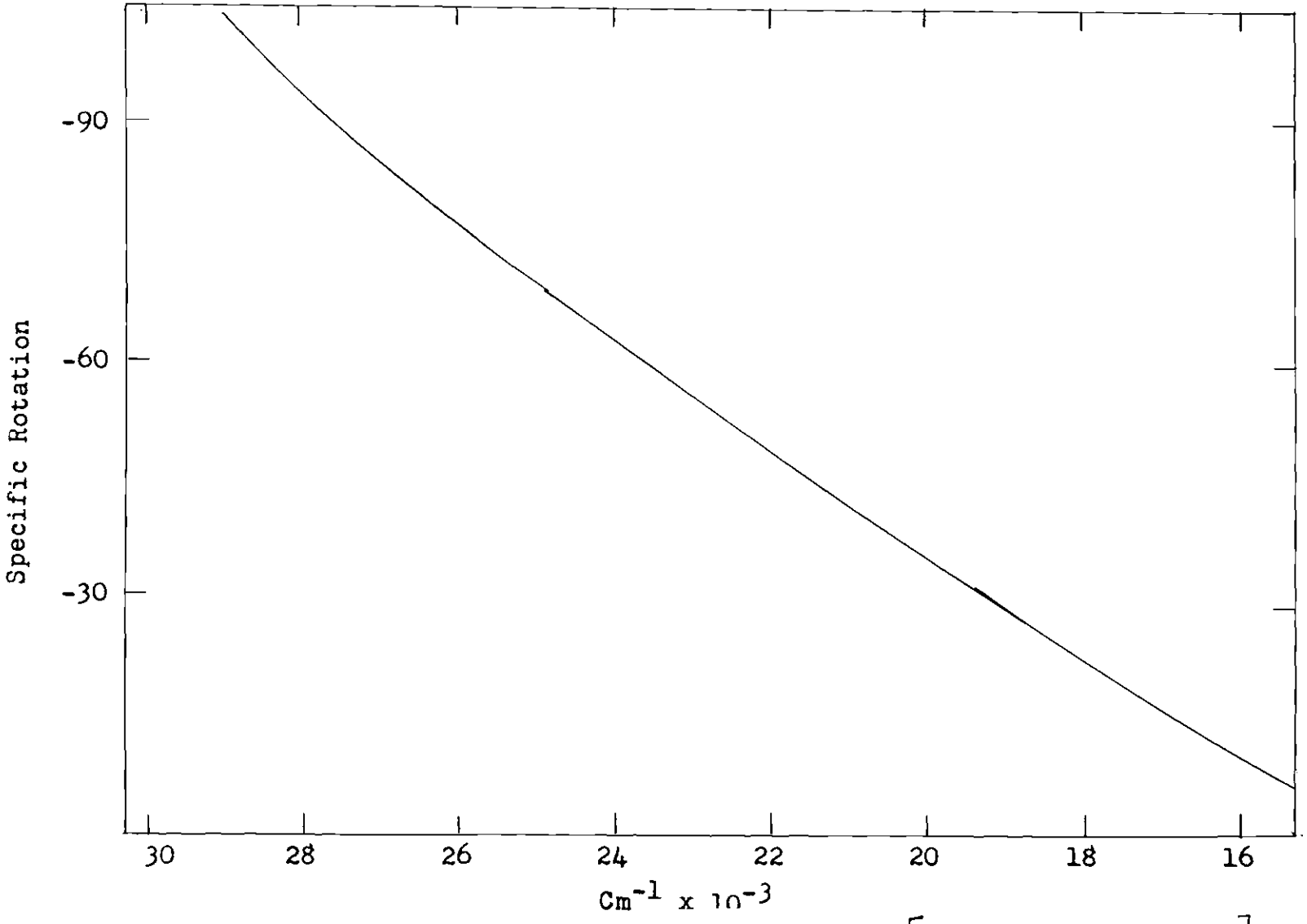


Figure 9. Optical Rotatory Dispersion Spectrum of $-[Co(cptdin)_3(CO_3)(H_2O)]Cl$

amine molecules have the same optical configuration.

The small difference in the rotation of the recovered amine in fractions two and three can also be attributed to the fact that this isomer is not as pure as the more insoluble isomer.

The Most Soluble Isomer (Fraction Four)

The visible spectrum of this fraction shows two maxima at the same positions as the spectra of the other three isomers. However, the intensity of the two maxima are not the same as in the other isomers; in this case the maximum at the shorter wavelength is much more intense than the one at longer wavelength. Although this fraction is a cobalt(III) complex, no further characterization work was done, since the fraction contains more than a single compound.

Some preliminary work, using paper chromatography, using methanol-water and acetone-water mixtures as solvents, show that there are at least two components in the mixture. The chromatograms showed that the separation with the above solvents was poor, and no large scale work-up of the fraction was attempted. One of the components is probably the soluble form of the dimeric species since the specific rotation of the soluble fraction is quite high. The mixture probably contains some complexes, which have very little difference in solubility, and which contain both optical isomers of the amine. It is also possible that there may be some geometrical isomers in this fraction.

CHAPTER V

DISCUSSION AND CONCLUSIONS

The investigation of trans-1,2-cyclopentanediamine complexes of cobalt(III) by Jaeger and Blumendal (5) was one of the most significant investigations of the stereospecific nature of metal complexes containing asymmetric ligands. The reinvestigation of this system by Royer and Phillips (15) in the light of Dwyer's work with the cobalt(III) complexes of d- and l-propylenediamine show that although Jaeger's conclusions as to the formula and structure of the complex were incorrect, the stereospecificity of the complexes formed was just as Jaeger had concluded.

The cobalt(III) complexes with trans-1,2-cyclopentanediamine reported by Royer and Phillips (15) have an unusual structure in which there are two differently coordinated amines in a single complex unit; three amine molecules functioning as a form of a tridentate ligand in that they bridge two cobalt nuclei and therefore are coordinated through both amine groups, and four other amines singly coordinated through a single amine group. Examination of molecular models suggested that perhaps if the number of bridging amines was decreased to two that it should be possible to form a binuclear complex in which the two bridging amines should be mirror images of one another without causing any steric hinddrance.

It would also be very desirable to be able to prepare and isolate the tris-cis-1,2-cyclopentanediamine cobalt(III) complexes. In this system, since a five-membered saturated carbon ring is relatively rigid and

cannot form the two enantiomers as in the case of the ethylenediamine and propylenediamine, the complex formed should contain a chelate ring of the envelope conformation in which all the hydrogens would be eclipsed. It would be of great interest to see what effect this has on the relative stability of the complex as compared to the ethylenediamine and propylenediamine complexes of cobalt(III). It would also be desirable to see what effect this has on the optical activity of the complexes which are formed.

It was with these thoughts in mind that this research was undertaken.

The preparation of the trans-1,2-cyclopentanediamine was done in the same manner as described by Jaeger (5), Cope (17), and Royer (15). An attempt was made to stereospecifically prepare the cis-1,2-cyclopentanediamine by a Schmidt reaction upon cis-1,2-cyclopentanedicarboxylic acid, but only negligible yields of amine were obtained. The amount of amine was insufficient to allow any characterization of the amine, or to prepare a sufficient amount of the cobalt(III) complex to allow its characterization. An attempt was made to separate the two geometrical amine isomers by a ligand exchange reaction after the method of Latterell and Walton (22); however, there was no detectable separation of the two geometrical isomers.

The inability to either stereospecifically prepare or to separate the geometrical isomers of the amine to obtain the cis amine prevented any investigation into the effect of the conformation of the chelate ring on the stability or optical activity of the cobalt(III) complexes.

Due to its high water solubility and its sensitivity to decomposition in both acidic and basic solution the purification of the

$[Co(cptdin)_3(CO_3)(H_2O)]Cl$ was relatively difficult. Separation by countercurrent distribution and then repeated fractional crystallization of the tartrate salt, conversion to the chloride salt, and fractional crystallization of these yielded four different fractions of different specific rotations. The most insoluble fraction had the highest specific rotation and the larger more soluble fractions had somewhat low specific rotations.

The amount of high rotation compound was too small to allow complete characterization. However, from the available infrared, analytical, and optical rotatory dispersion data, the compound is thought to be a binuclear complex with a structure very similar to the structure of the $[Co_2(cptdin)_7(H_2O)_2]Cl_6 \cdot 2H_2O$ and with a probable formula of $[Co_2(cptdin)_6(CO_3)_2]Cl_2$.

The optical rotatory dispersion spectrum shows a relatively large Cotton effect associated with the long wavelength absorption maximum in the visible spectrum. This indicates that the complex should contain bidentate ligands. If all the amine molecules are of the <u>trans</u> configuration and incapable of chelation, then the only means of making them act as a bidentate ligand is to allow them to bridge two cobalt nuclei.

This gives an overall apparent molecular weight of 303 which is in reasonably good agreement with the experimentally determined apparent molecular weight of 290.

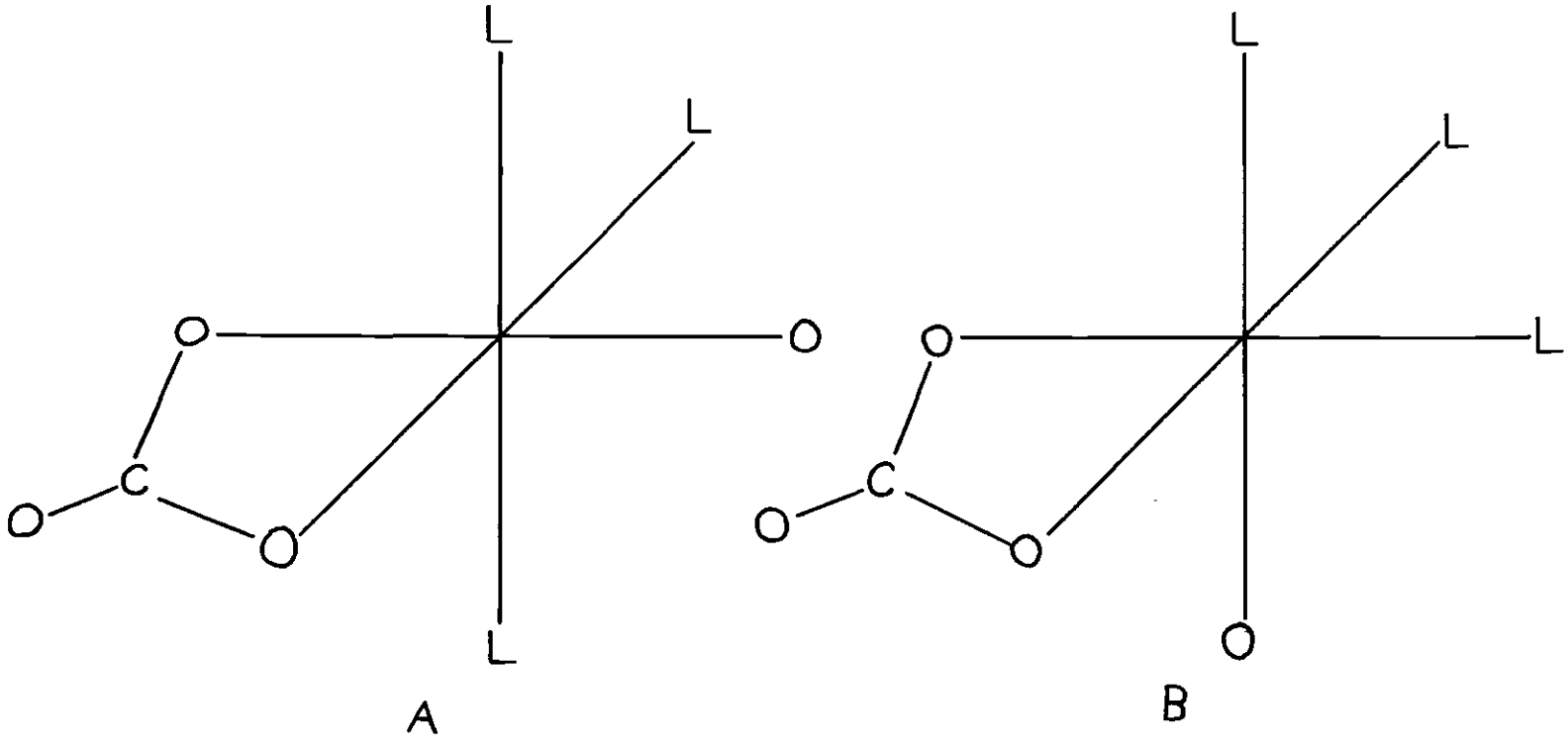
If one assumes the most symmetrical structure for the compound $[Co_2(cptdin)_6(CO_3)_2]Cl_2$, then there should be two bridging amine molecules and four monodentate amine molecules. It should be possible in this case for the two bridging amine molecules to be mirror images.

However, insufficient material was available to determine the optical configurations of the coordinated amines. However, it is believed, due to the high optical rotation and the observed Cotton effect (Figure 4), that all the amines are of the same optical configuration in the complex.

The two low rotation isomers also had a one to one cobalt to chloride ratio, indicating the compound contains coordinated carbonate ion. Analysis of the infrared spectrum after deuteration of the amine hydrogens showed that the carbonate was functioning as a bidentate ligand. The infrared spectra also showed the presence of coordinated water in the complex. Further analytical data showed that there were three coordinated amine molecules per cobalt. A determination of the apparent molecular weight gave a value of 229 assuming the complex was a one to one electrolyte; indicating that the complex was a mononuclear species consistent with the formula $[Co(cptdin)_3(CO_3)(H_2O)]Cl$. The apparent molecular weight data rule out a dimeric or more highly associated species since they would have had apparent molecular weights of 300 or greater.

At this point there are only two possible structures that will fit the above data (Figure 10). The two structures in Figure 10 have coordination spheres which are the same as those reported by Douglas and Yamada (7) for the tris-amino acid complexes of cobalt(III) (Figure 11). Structure A has a coordination sphere similar to the α isomer of the tris-amine acid complex and structure B having a coordination sphere similar to the β isomer.

Investigation of the visible spectrum of $[Co(cptdin)_3(CO_3)H_2O)]Cl$ (Figure 6) shows two symmetrical maxima. One at 530 millimicrons and



L = cptdin

Figure 10. Coordination Sphere of $[Co(cptdin)_3(CO_3)(H_2O)]Cl$

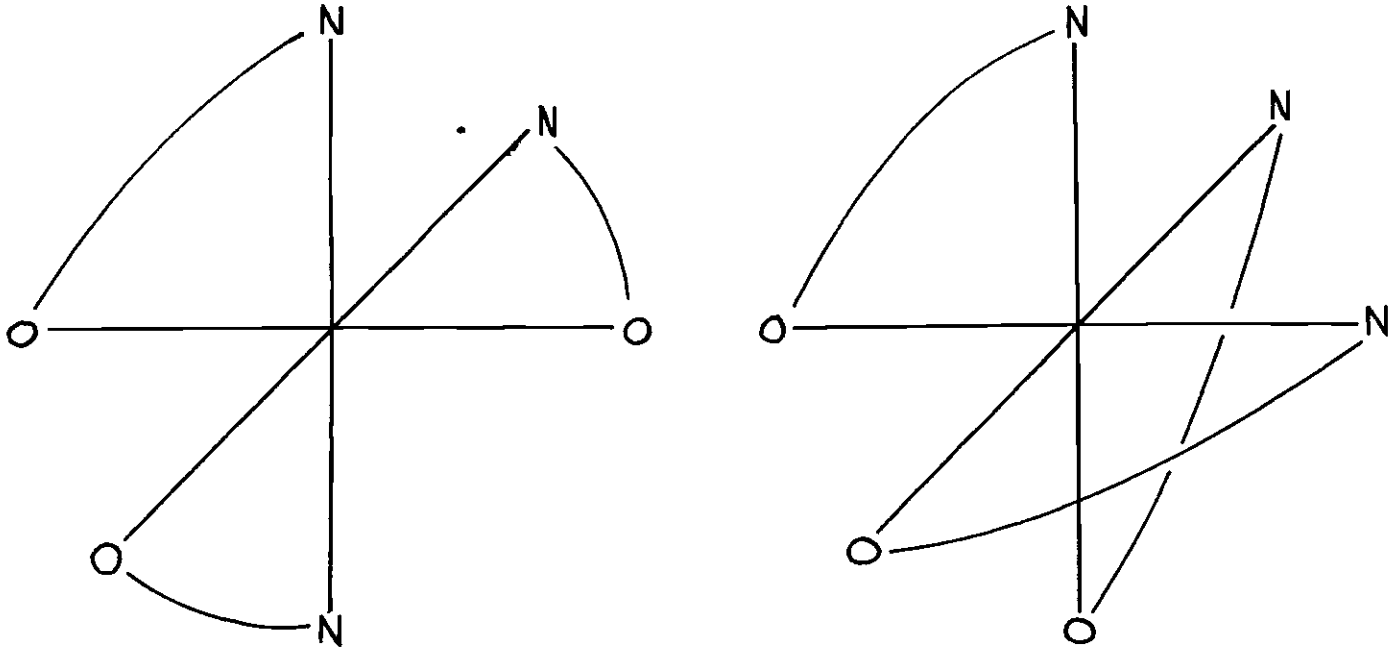


Figure 11. Coordination Sphere of the α and β Isomers of the Tris-Aminoacid Cobalt(III) Complexes

the other at 370 millimicrons, with the maxima at the longer wavelength being slightly more intense than the one at shorter wavelength. The visible spectrum (Figure 6) of the β isomer of the tris-amino acid complex is very similar to this having maxima at 523 and 374 millimicrons with the long wavelength maxima being more intense.

In the case of the α isomer of the tris-amino acid complex the maxima in the visible spectra (Figure 6) occur at 548 and 367 millimicrons and the long wavelength peak is less intense than the one at shorter wavelength. The maxima at the longer wavelength is also quite asymmetrical in the α isomer.

From the above considerations structure B is proposed to be the correct structure for $[Co(cptdin)_3(CO_3)(H_2O)]Cl$.

The low rotations and lack of a Cotton effect in the optical rotatory dispersion curves are in agreement with the work of Larsen and Olsen (24), who have reported that cobalt(III) complexes which contain an optically active amine which does not function as a bidentate ligand do not exhibit any Cotton effect in the circular dichroism curves.

From the specific rotation of the recovered amine from fraction two, the more insoluble low rotation fraction, one can calculate the expected specific rotation of the complex if the total optical rotatory power is attributed only to the amine. The specific rotation of the free amine was +42 degrees. The specific rotation of the complex calculated from the rotation of the amine is +27 degrees. The experimentally observed rotation was +31 degrees, in reasonably good agreement with the calculated value.

The more soluble low rotation fraction does not give results which

are in quite as good agreement. The observed rotation of the amine was -39 degrees which gives a calculated rotation for the complex of -25 degrees. The observed rotation of the complex was -30 degrees. The somewhat low rotation of the recovered amine can be attributed to contamination by the other isomers since this was the next to most soluble fraction.

The most soluble fraction was not characterized due to the failure of the complex to form any slightly soluble salts which could be separated by fractional crystallization or by other means. The visible spectrum of this fraction also gave two maxima, one at 530 millimicrons and the other at 370. However, in this case the long wavelength maxima was much less intense than the one at shorter wavelength. This suggests that this fraction probably contains compounds with coordination spheres somewhat different than those in the other three complexes. Paper chromatography of the more soluble fraction shows the presence of two components.

It has been found that trans-1,2-cyclopentanediamine is very strongly stereospecific in the formation of complexes with cobalt(III). It would be interesting to see if the coordinated carbonate group could be replaced by an amine of the opposite configuration of those in the complex. It would also be of interest to pursue Larsen and Olsen's (24) tentative proposal that chelation is necessary for the observation of a large Cotton effect.

It would also be desirable to prepare a chelating diamine ligand in which the chelate ring would of necessity be planar. A ligand which might serve this purpose and which has been previously prepared is the

cis-1,2-cyclobutanediamine. It might also be of some interest to attempt other methods to prepare the cis-1,2-cyclopentanediamine, since there is no reported synthesis of this particular diamine in the literature.

It might also be possible to separate the most soluble fraction by countercurrent distribution of the d-tartrate salt or perhaps some other somewhat more insoluble salt.

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* Abbreviations used herein follow the form appearing in Chemical Abstracts, 50, 1 J (1956).

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